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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G01R 27/04

A1

(11) International Publication Number: WO 99/13346

(43) International Publication Date: 18 March 1999 (18.03.99)

(21) International Application Number: PCT/US98/18736

(22) International Filing Date: 9 September 1998 (09.09.98)

(30) Priority Data:
08/926,731 10 September 1997 (10.09.97) US

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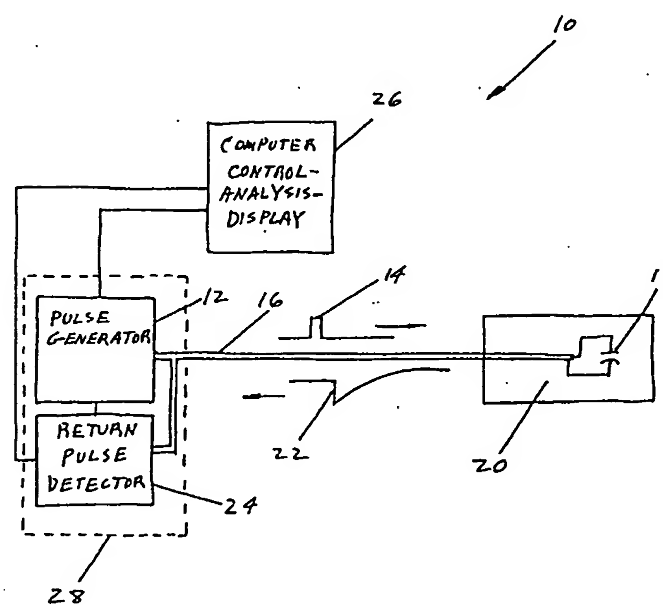
(81) Designated States: CA, DE, GB, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METHOD AND APPARATUS FOR IN-SITU MEASUREMENT OF POLYMER CURE STATUS



(57) Abstract

An apparatus and method for determining the cure state of thermosetting polymers using time domain reflectometry. A miniature capacitor (18) is constructed at the end of a controlled transmission line (16) which is immersed in the curing polymer (20) so that the polymer (20) is the dieletric of the capacitor (18), and step function voltage pulses (14) are fed to the transmission line, while the reflected signal (22) from the line (16) is monitored. The amplitude and decay characteristics of the reflected signals (22), which are related to the degree of cure and the viscosity, respectively, are fed to a computer (28) for interpretation and display (26).

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BACKGROUND OF THE INVENTION

This invention deals generally with electrical measuring and testing, and more specifically with the determination of the non-electric property of the state of cure of a thermosetting polymer by the use of time domain reflectometry.

The degree of cure of thermosetting polymers is of considerable interest in industry because the cure status determines the strength of a part and also whether it can be subjected to subsequent manufacturing processes. However, since the cure status of the internal portion of a part can not be evaluated visually, considerable effort has been expended to find methods to accurately evaluate the cure state.

Several electrical methods to determine cure state have been used. Among them are the measurement of impedance (U.S. Patent 5,432,435 to Strong et al), reflection of continuous microwave energy (U.S. Patent 5,059,914 to Lacombe et al), and dielectric properties (U.S. Patent 4,777,431 to Day et al). Carrozzino et al have also performed laboratory tests (noted in Polymer Engineering And Science, March 1990, Vol. 30, No. 6, p 366) on the use of time domain reflectometry to evaluate the degree of cure. However, Carrozzino concluded that such an approach had poor accuracy and repeatability, and the publication did not disclose the use of in-situ sensors or the measurement of viscosity.

SUMMARY OF THE INVENTION

The present invention provides a time domain reflectometry apparatus which furnishes highly accurate and repeatable measurements of the viscosity and percent of cure of polymers. The invention combines the simplicity of electrical sensing with miniaturization available from high frequency techniques in a time domain reflectometry measuring device. Such an apparatus is usable for in-situ monitoring of the cure status of composites, and is important for overcoming quality control problems, increasing production speed, and improving the uniformity of composite

manufacture, especially in critical structures.

In the preferred embodiment of the invention, a sensor embedded within the part being constructed receives and reflects a fast rise time pulse, and the reflected transient signal relates to the dipole rotation occurring in the microwave frequency range for a particular epoxy dipole. Because of this phenomenon, the reflected signal can be directly related to viscosity and percent of cure. In experimental tests, changes in the signal have been followed during processing and compared to other test methods to establish information in regard to the relationship of the reflected signal to the state of cure and to the viscosity.

The sensor is a miniature capacitor constructed at the end of a miniature transmission line which is immersed in the curing polymer. Step function voltage pulses are fed to the transmission line, and the reflected signal from the transmission line is monitored. The amplitude of the reflected pulse signals, which is related to the degree of cure, and the decay characteristics of the reflected pulse signals, which are related to the viscosity, are then fed to a computer for interpretation and display.

The invention thereby furnishes a real time measurement of the state of cure of the polymer, and the transmission line and sensor, which remain in place after the material is cured, can actually be used with the same signal generator and signal processing system to later check for cracks or discontinuities which might develop in the cured part at a later time.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a simplified schematic diagram of the preferred embodiment of the invention.

FIG. 2 is a partial cross section side view of the sensor and transmission line of the alternate embodiment of the invention.

FIG. 3 is a top view of the sensor and transmission line of an alternate

embodiment of the invention.

FIG. 4A and 4B are graphs of the typical variations in the reflected pulse with time as polymers cure.

FIG. 5 is a graph showing how the decay of reflected pulses changes with viscosity.

FIG. 6 is a graph showing how the reflected pulses change with reduced dipole rotation as cure progresses.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 is a simplified schematic diagram of the preferred embodiment of cure monitoring apparatus **10** of the invention in which pulse generator **12** supplies step function incident pulse **14** to transmission line **16**. Capacitor sensor **18**, which is located at the remote end of transmission line **16**, is immersed within curing polymer **20** and reflects return pulse **22** back to pulse detector **24**. The timing of pulse generator **12**, the analysis of return pulse **22**, and the display of the test parameters and results are performed by computer **26**.

The parameters of the reflected pulse which indicate the viscosity and cure status of polymers are the variations in the decay time for viscosity and variations of the amplitude for percent of cure. These are affected by the dipole rotation spectrum of the polymer. Changes in the reflected pulse parameters are actually indications of a more sophisticated change in frequency characteristics of the polymer, so that measurements of the changing characteristics of the reflected pulse actually measure changes in the materials' frequency characteristics, such as changes in loss peak frequency.

The frequency characteristics can also be measured by direct application of a signal sweeping through a wide spectrum of frequencies and spectrum analysis of the returning signals, but such an arrangement, although perhaps easier to interpret, is

more difficult to measure. The pulse technique used in the invention uses a fast risetime pulse, a few nanoseconds or less, which is well understood in the art to actually include the same wide spectrum of frequencies. The reflected pulse then actually includes the desired frequency information, and a Fourier Transform can also be used to arrive at the dipole rotation spectrum and the loss peak frequency.

However, the desired information of percent cure and viscosity can also be secured by making simple measurements on the reflected pulse.

The invention's preferred embodiment of a method of measuring cure status, that is, viscosity and percent of cure of a polymer, is:

A) immersing at least one end of a transmission line into a polymer which is curing, with a capacitor connected to the immersed end of the transmission line, and the capacitor constructed so that its dielectric is the polymer into which it is immersed;

B) generating one or more step function voltage pulses and feeding the pulses to the transmission line;

C) receiving reflected pulses back from the capacitor at the end of the transmission line; and

D) analyzing changing characteristics of the reflected pulses to establish the viscosity and status of cure of the polymer in which the transmission line is immersed.

In most installations pulse generator **12** and pulse detector **24** are actually included in one unit, sampling head **28**. In the preferred embodiment, sampling head **28** is a Hewlett Packard model 54750 Time Domain Reflectometry Oscilloscope which has a 35 ps input transient and a 20 GHz detection bandwidth.

In the preferred embodiment, incident pulse 14 is 200 millivolts, with a rise time of 35 picoseconds. The pulse length and repetition rate are not critical as long as

the pulse length is long enough and the repetition rate is slow enough so that they do not result in additional pulses being generated during the 1 nanosecond to 10 microseconds after the beginning of the reflected pulse when pulse analysis is being performed. The desirable pulse risetime and detector sampling resolution is in the range of 1 picosecond to 10 nanoseconds. Pulses can also be produced in bursts to produce a lower effective frequency so that data is transferred to computer **26** at a lower effective rate.

Transmission line **16** can be any type of controlled impedance high frequency transmission line. As illustrated in FIG. 2 and FIG. 3, this includes both coaxial and flat ribbon, so called "Stripline", transmission lines. For the preferred embodiment, a .25 mm, 50 ohm, flat ribbon line is used. The length of transmission line **16** was chosen to avoid ¼ wave resonance, and the line itself must be free of connectors which add undesirable signal distortions and reflections.

Sensor **18**, which is immersed in curing polymer **20**, is essentially a miniature capacitor whose fringing electric field extends into the polymer. In the preferred embodiment, it is a 1 to 2 picofarads capacitance formed near end **30** of transmission line **16**, as shown in FIG. 2, but it is practical to use a capacitance in the range of 1 to 10 picofarads.

FIG. 2 is a top view of Sensor **32** and transmission line **34** of the preferred embodiment of the invention. Sensor **32** and transmission line **34** are constructed as planar stripline components. Such devices are conventionally fabricated on a thin insulating substrate, and center conductor **36** is centered between coplanar ground planes **38**. Transmission line **34** of the preferred embodiment of FIG. 2 is constructed with a 50 ohm impedance along the transmission path, with an interlaced finger structure **40** at the end of transmission line **34** to form capacitor **42**.

Transmission line **34** and capacitor **42** are fabricated on copper laminated

teflon sheets of .1 to 1 millimeter thickness, and the pattern is made by photolithography and chemical etch methods. The material between the fingers 40 is completely etched away so that it will be replaced by the curing polymer within which capacitor 42 will be immersed. If a greater capacitance is desirable, the fingers 40 can easily be made longer, thus increasing the effective surface of the capacitor. In fact, one way in which the stripline capacitor is constructed is to manufacture the capacitor section 42 of stripline transmission line 34 much longer than will be needed and to merely cut it down to secure the desired capacitance in the 1 to 10 picofarad range.

In an alternate embodiment shown in FIG. 3, capacitor 18 is formed on transmission line 16 by first removing a short length of outer coaxial shield 46, leaving a 2 to 3 mm length of insulating sleeve 48 exposed. The entire surface of exposed insulating sleeve 48, including end 49, is then covered with electrically conductive layers 50 and 52, which are shown in cross section. Conductive layers 50 and 52 are typically metal, although they can be other electrically conductive materials. They can be applied using conventional methods, such as evaporation or chemical plating. At this stage of construction, conductive layers 50 and 52 are joined because they have been formed as one continuous layer, and they actually create a short circuit between center conductor 54 and outer shield 46. However, the thickness of the conductive layers is not critical since there will be no significant current flow through them.

The final stage of the construction of capacitor 18 is simply forming gap 56 along the length of insulating sleeve 48 and separating conductive layers 50 and 52. Gap 56 extends through conductive layers 50 and 52 and insulating sleeve 48 to center conductor 54, and thus destroys the previously formed short circuit. Gap 56 thereby functions as the dielectric space of a capacitor whose "plates" are conductive layers 50 and 52, which are connected to inner conductor 54 and outer shield 46, respectively.

Gap 56 is eventually filled by the curing polymer within which capacitor 18 is immersed. Gap 56 is formed by conventional methods such as laser cutting, or chemical etch methods. If a greater capacitance is desirable, gap 56 can be formed as two interlaced finger structures, thus increasing the effective surface of capacitor 18.

FIG. 4 A and B are graphical representations of the typical variation in amplitude of reflected signal 22 (FIG. 1), in millivolts, against cure time, in minutes, as polymer 20 (FIG. 1) goes through a normal curing process. The readings for FIG. 4A were taken at 1 nanosecond after the start of the reflected pulse. and are therefore close to the peak of the reflected pulse. The readings for FIG. 4B were taken at 50 nanoseconds after the start of the reflected pulse, and are therefore well into the decaying "tail" of the pulse. The material used in these tests was Hexcel 8552. The curve is essentially similar for most thermosetting polymers. The temperature at which the samples were held during the tests was between 25 - 175 degrees Celsius. With such data available to computer 26 of FIG. 1, it is a simple task to establish when a polymer has experienced equivalent signal reductions and therefore to establish the state of cure by comparing the changing characteristics of the reflected pulses to characteristics of pulses reflected during previous controlled tests of curing polymers. This is easily accomplished by the use of computer 26 whose memory can include the previous test results. Moreover, controlled tests can be run and put into memory for any new type of material so that later production testing equipment can evaluate such new materials.

However, previous test results are not a necessity. A preferred method of analysis is to measure and compare the changing amplitudes at two points on the decaying tail of the pulse for a series of reflected pulses over a period of time. As indicated in FIG. 4, typically, one of these observation points on the reflected pulses is less than 10 nanoseconds after the reflected signals begin, and the other observation

point on the reflected pulses is greater than 15 nanoseconds after the reflected pulses begin. These time ranges are chosen because, as can be seen on FIG. 5, they exclude the region in which change is minimal for the viscosity indicator factor.

FIG. 5 is a graph showing the manner in which the reflected pulses change as viscosity of the typical polymer changes. As can be seen from the two curves on FIG. 5, as viscosity increases as the polymer cures, the amplitudes of the reflected pulses are decreased at short times and increased at long times. A simple ratio of the amplitudes at the short time measurement point and at the long time measurement point can therefore indicate the change in viscosity of the polymer.

It is important to recognize that the curing process is usually preceded by a period in which the temperature of the polymer is increased, and during this time, when no curing is taking place but the viscosity is decreasing, the ratio of amplitude of the signal at short times to the amplitude of the signal at long times is an indicator that this process is taking place.

FIG. 6 is a graph showing the manner in which the reflected pulses change with reduced dipole rotation as cure of the typical polymer progresses. In this case the amplitudes of the reflected pulses are reduced at all points. In fact, the completion of the curing process can be determined when this reduction in amplitude is no longer occurring, indicating that the cure is complete. It is interesting to note that the absolute amplitude of reflected pulses at this end point of solidification should always be approximately the same for the same sensor and the same material. Therefore, in a production situation, if the amplitude reduction has stopped, but the absolute value of the amplitude is not within an appropriate range, it is an indication that there is an undesirable variation in the material.

The present invention thereby provides an accurate and reliable means to evaluate cure status of various polymers, and is capable of performing the task in

either the laboratory or the production environment.

It is to be understood that the form of this invention as shown is merely a preferred embodiment. Various changes may be made in the function and arrangement of parts; equivalent means may be substituted for those illustrated and described; and certain features may be used independently from others without departing from the spirit and scope of the invention as defined in the following claims.

I CLAIM:

1. A method of measuring viscosity and percent of cure of a polymer comprising:

immersing at least one end of a transmission line into a polymer which is curing, with a capacitor connected to the immersed end of the transmission line, and the capacitor constructed so that its dielectric is the polymer into which it is immersed;

generating at least one step function voltage pulse and feeding it to the transmission line;

receiving a reflected pulse back from the capacitor at the end of the transmission line; and

analyzing the characteristics of the reflected pulse to establish the condition of the polymer in which the transmission line is immersed.

2. A method of Claim 1 wherein analyzing the reflected pulse comprises comparing characteristics of the reflected pulse to characteristics of pulses reflected during previous tests of curing polymers.

3. A method of Claim 1 further including generating a series of pulses and analyzing the reflected pulses by comparing the changing amplitudes of the reflected pulses over time to determine the state of cure of the polymer.

4. A method of Claim 1 further including generating a series of pulses and analyzing the reflected pulses by comparing the changing decay curves of the reflected pulses over time to determine the viscosity of the polymer.

5. A method of Claim 1 further including transforming the reflected pulses into the frequency domain and analyzing the resulting frequency of the dipole rotation spectrum to determine the viscosity of the polymer.

6. A method of Claim 1 further including transforming the reflected

pulses into the frequency domain and analyzing the resulting loss peak frequency to determine the state of cure of the polymer.

7. A method of Claim 1 wherein analyzing the reflected pulses comprises comparing over time the amplitudes of the reflected pulses at a point on the reflected pulses which is less than 10 nanoseconds after the reflected pulses begin to the amplitudes of the reflected pulses at a point on the reflected pulses which is greater than 15 nanoseconds after the reflected pulses begin.

8. An apparatus for measuring viscosity and percent of cure of a polymer comprising: a pulse generator generating at least one step function voltage pulse;

a transmission line connected to and receiving pulses from the pulse generator, with one end of the transmission line immersed in a polymer which is curing;

a capacitor connected to the immersed end of the transmission line and also immersed in the polymer which is curing, the capacitor being constructed so that its dielectric is the polymer into which it is immersed;

a pulse detector connected to the transmission line and receiving a signal from the transmission line which is a pulse reflected from the immersed capacitor;

and an analyzer means interconnected with the pulse detector, the analyzer means being capable of measuring the changes in reflected pulses as the polymer cures.

9. An apparatus of Claim 8 wherein the pulse generator and the pulse detector are included in the same instrument.

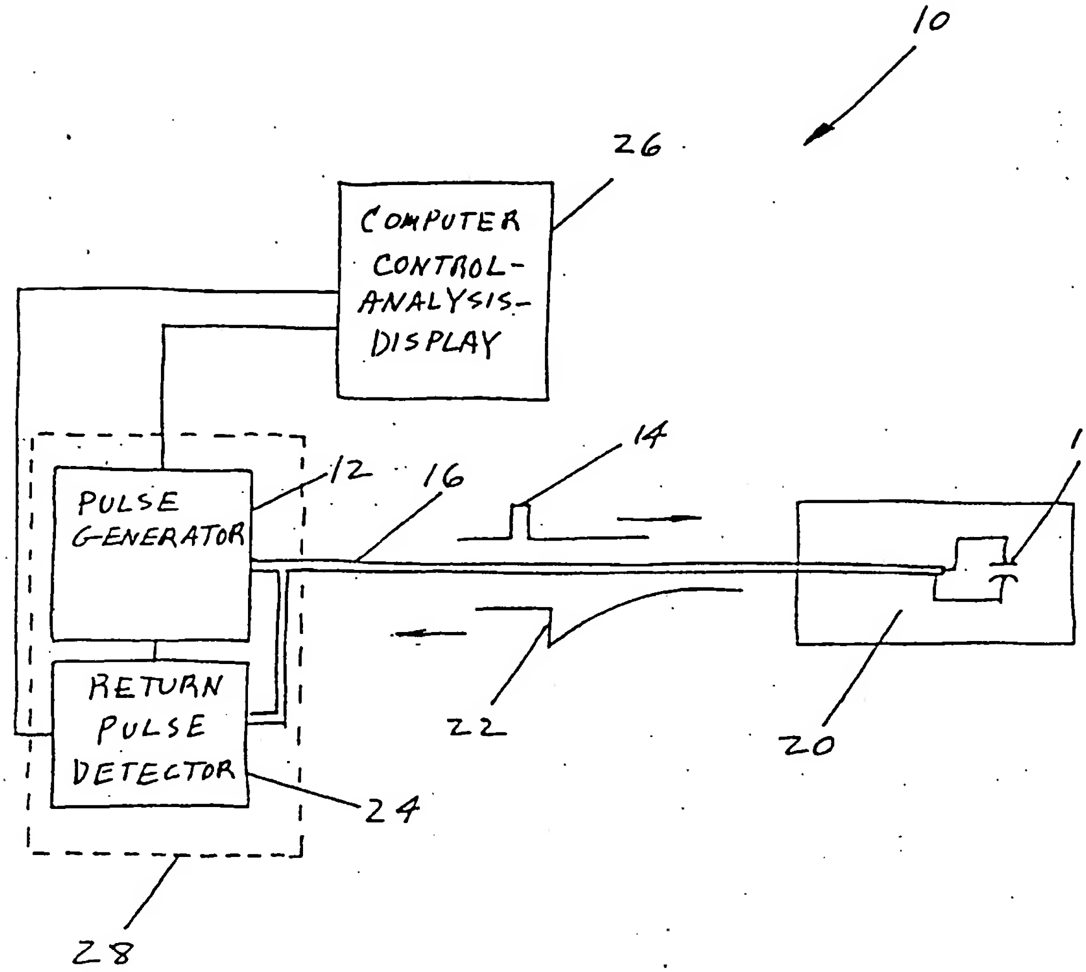
10. An apparatus of Claim 8 wherein the transmission line is a flat line with a central conductor, insulating strips on both sides of the central conductor and outer conductors on the opposite sides of the insulating strips from the central conductor, and the capacitor is integrated into the transmission line by forming an interlaced finger structure adjacent to the end of the transmission line.

11. An apparatus of Claim 10 wherein the central conductor and the outer conductors adjacent to the end of the transmission line form two interlaced finger structures so that the central conductor and the outer conductors have an increased area adjacent to the end of the transmission line..

12. An apparatus of Claim 8 wherein the transmission line is coaxial with an inner conductor, an insulator, and an outer conductor,

and the capacitor is integrated into the transmission line by forming a gap in the insulator and outer conductor adjacent to the end of the transmission line. and connecting the separate part of the outer conductor to the central conductor of the cable.

13. An apparatus of Claim 8 wherein the capacitance of the capacitor is in the range of between 1 and 10 picofarads.


10
26
COMPUTER
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PULSE
GENERATOR
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FIG. 1

Figure 2 – Stripline Sensor

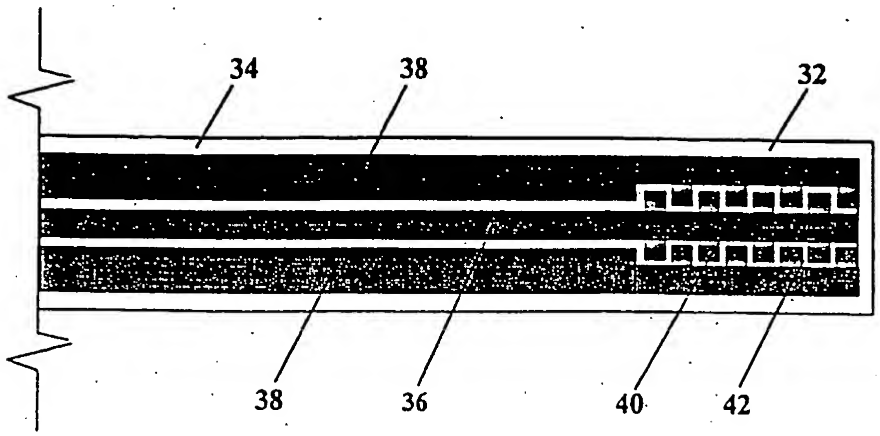


Figure 3 – Coaxial Sensor

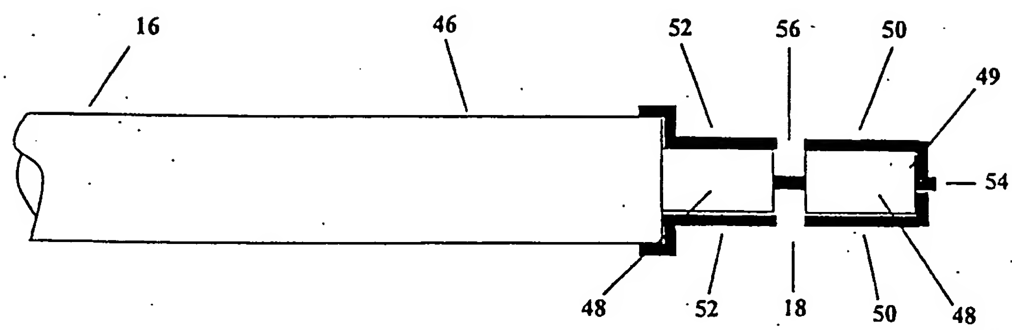


Fig 4a - Reflected Pulse Amplitude at 1.0 Nanoseconds

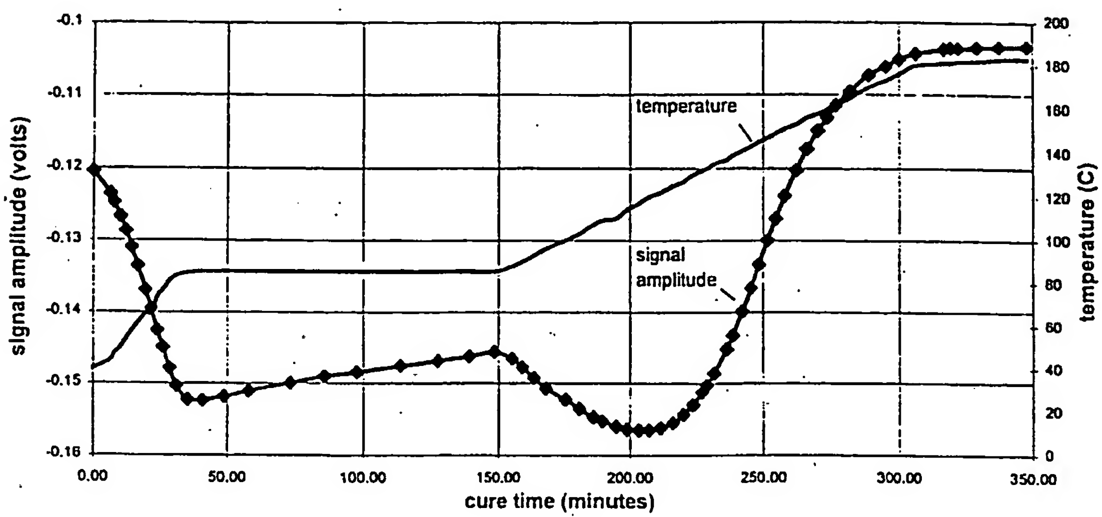
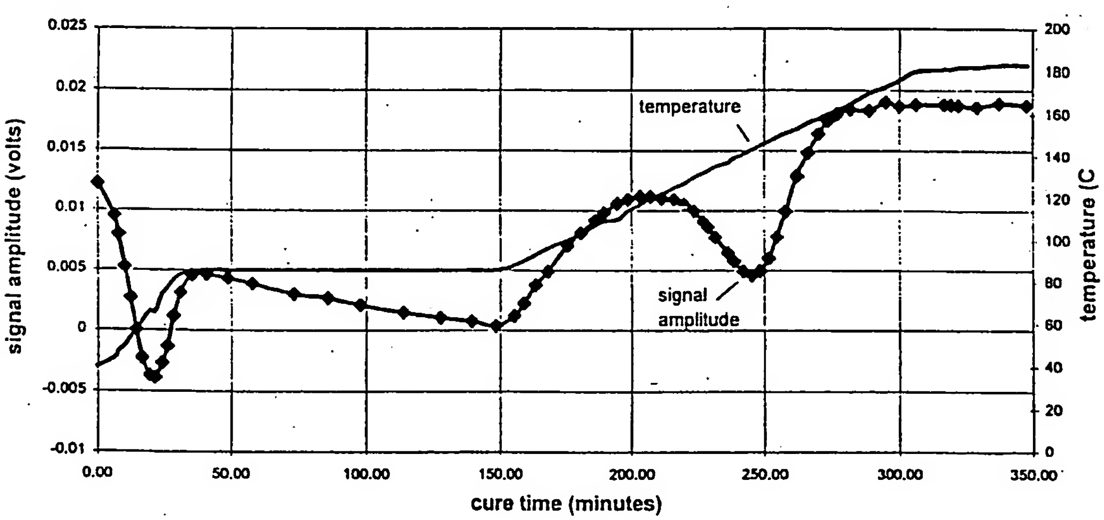
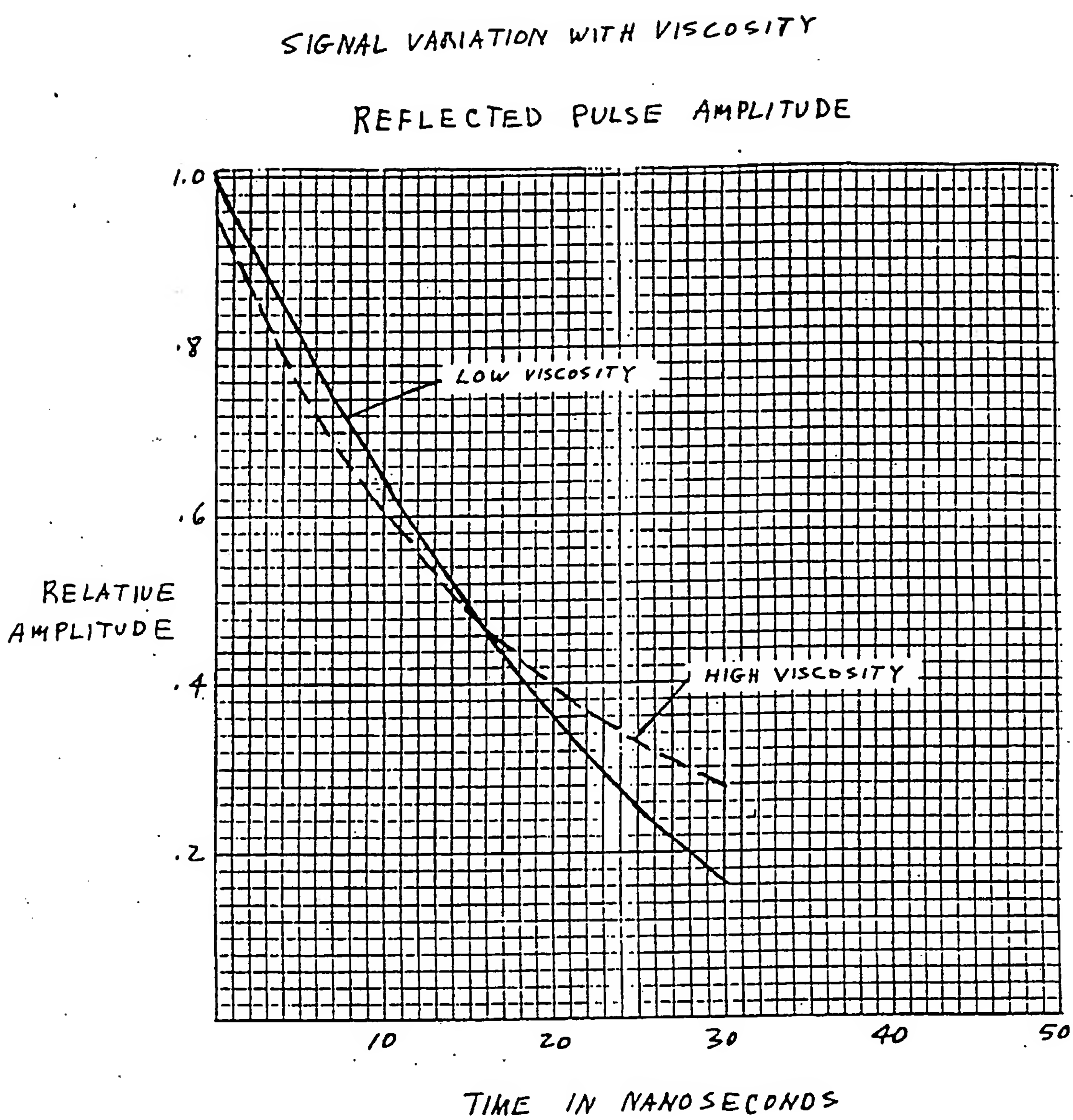


Fig 4b - Reflected Pulse Amplitude at 50 Nanoseconds

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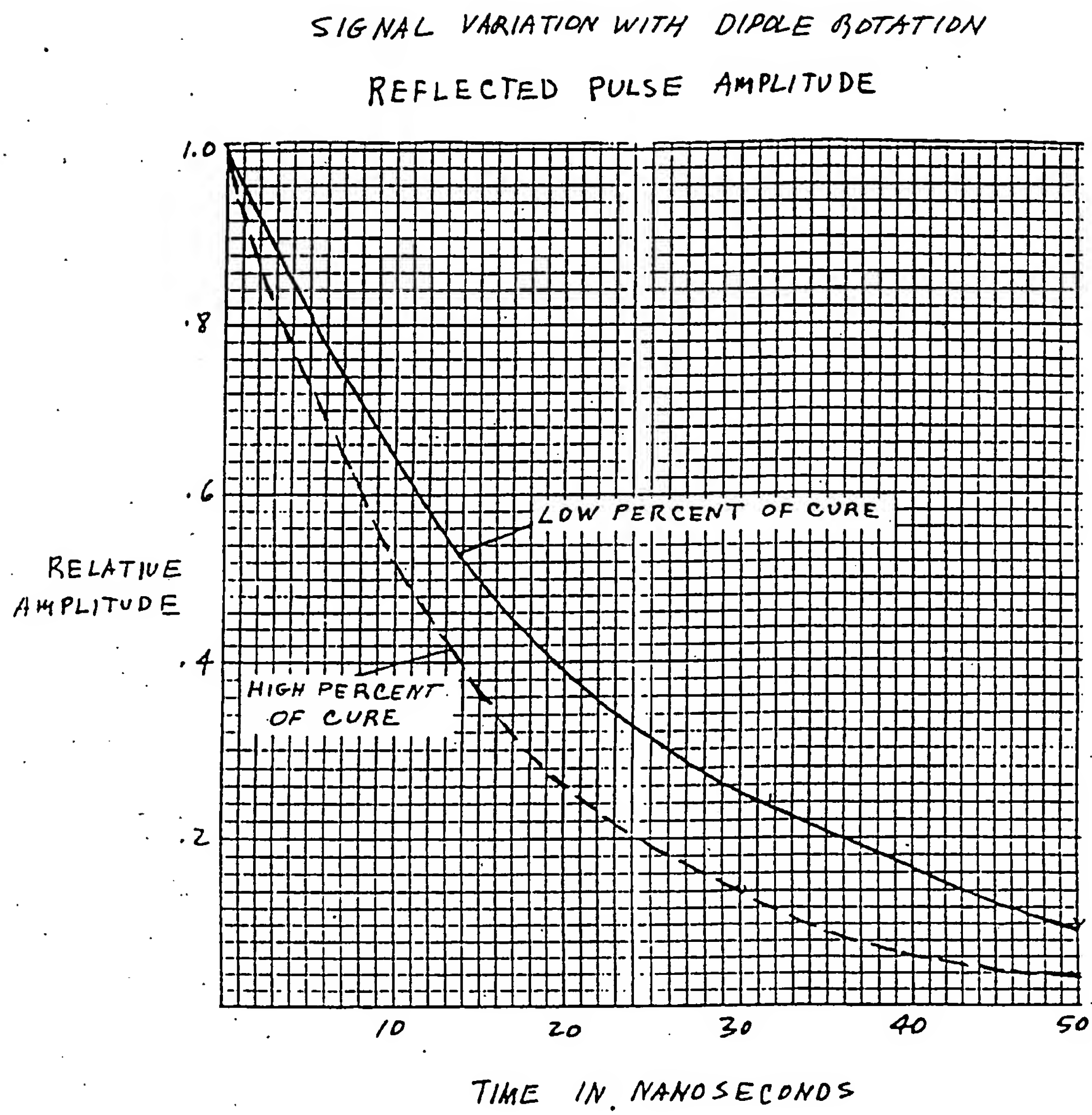
50
TIME IN NANOSECONDS

FIG. 5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.4
.2
RELATIVE AMPLITUDE
LOW PERCENT OF CURE
HIGH PERCENT OF CURE
10
20
30
40
50
TIME IN NANOSECONDS

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/18736

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G01R 27/04
US CL :324/637, 642, 71.1
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 324/632, 637, 639, 640, 642, 643, 646, 71.1; 73/54.41

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,779,452 A (COHEN-TENOUDJI et al) 25 October 1988, (25/10/88), see Fig. 5.	1-13
A	US 5,334,941 A (KING) 02 August 1994, (02/08/94), see Figs. 1-8.	1-13
A,P	US 5,744,971 A (CHAN et al) 28 April 1998, (28/04/98), see FIgs. 1 and 2.	1-13
A,P	US 5,748,002 A (SCOTT et al) 05 May 1998, (05/05/98), see Figs. 1-6.	1-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

26 OCTOBER 1998

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